CHEMISTRY CAT II

How is aluminium produced by electrolysis and what are the implications for society?

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Aluminium, the third most abundant element on the earth's surface[1] has many useful chemical properties which is why it's widely used in building, transport, machinery and packaging. The annual production of aluminium in the Western World is around 14.2 million tonnes[2]. This report outlines how aluminium is produced from alumina using electrolysis, the redox reactions involved and applies Faraday's Laws with relevant stoichiometry to determine the approximate efficiency of this process.

Electrolysis

Electrolysis involves the passage of an electric current through a conducting liquid[3]. It takes place in a Hall-Heroult cell, named after the two scientists who discovered the process. Electrolytic cells consist of a current travelling from anode, to cathode through an electrolyte (conducting liquid).

The reason for early problems with the production of aluminium is shown by the electrochemical series. If in an aqueous solution, the possible cathode reactions are:

$$2H^{+}_{(aq)}+2e^{-} \rightarrow H_{2(g)}$$

$$Al^{3+}_{(aq)}+3e^{-} \rightarrow Al_{(s)}$$ [4]

The hydrogen reaction is higher in the electrochemical series, therefore this reaction is favoured at the cathode as hydrogen ions are more easily reduced.

It's necessary for the electrolyte to consist of a melt of a compound containing aluminium. The cheapest compound is alumina, however it melts at 2020°C [5] requiring massive amounts of energy. Cryolite, Na_3AlF_6 was the compound discovered by Hall and Heroult in 1886 allowing electrolysis to occur at 950°C [6] (melting temperature) thus reducing energy costs.

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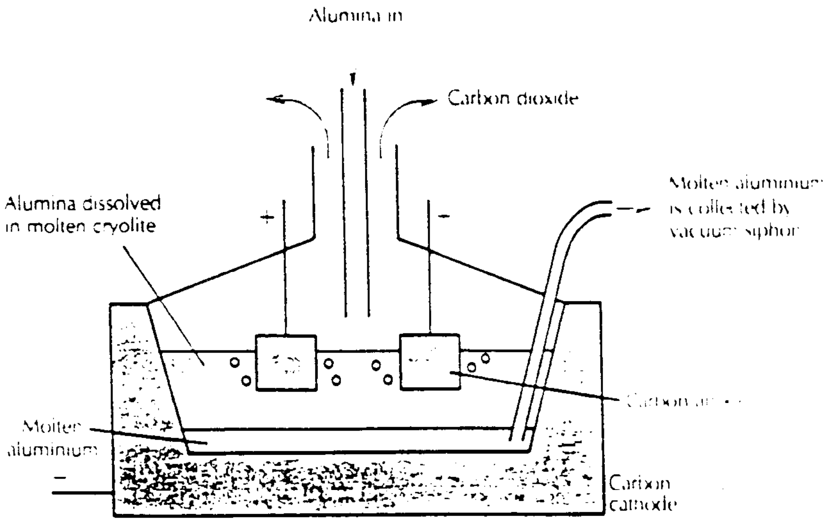
[1] Ross B. The Chemistry of Aluminium p10.
[2] Aluminium, mine to metal [poster]
[3] Commons C. Chemistry Two p127
[4] Commons C. Chemistry Two p211
[5] Electrodeposition of Metals
[6] Electrodeposition of Metals



The Hall-Héroult cell used to extract aluminium from alumina.

The diagram shows a typical cell or 'pot', lined with carbon, either anthracite (black coal) or graphite, acting as the cathode. The more recent graphitised blocks have increased cell life to around seven years and improved energy efficiency by reducing the voltage drop across the cathode[7]. The electrolyte above this, is 80% molten cryolite Na_3AlF_6 with additives of aluminium fluoride AlF_3, calcium fluoride CaF_2 and occasionally lithium fluoride LiF or magnesium fluoride MgF_2[8]. The fluorides are added to lower the melting point and improve electrical properties of the melt[9].

The anodes, also made from carbon, are multiple blocks consumed during the process, to reduce cost. The overall reaction without the consumption of carbon is:

$$Al_2O_{3(s)} \rightarrow 2Al_{(s)} + \tfrac{3}{2}O_{2(g)} \qquad E^\circ = -2\cdot 2V$$ [10]

With the consumption of carbon, the reaction is:

$$2Al_2O_{3(s)} + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)} \qquad E^\circ = -1\cdot 17V$$ [11]

The second equation uses almost half the electrical energy than the first. The total amount of energy used in the equations is equal, as chemical energy is used to consume the carbon. However, as carbon is reasonably cheap, the cost is reduced.

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[7] Nixon J.C. Aluminium Extraction p19
[8] Ross B. The Chemistry of Aluminium p4
[9] Ross B. The Chemistry of Aluminium p4
[10] Electrodeposition of Metals
[11] Ross B The Chemistry of Aluminium p4

The prebaked blocks suspended in the pot, form the positive electrode of the cell and are lowered as they are consumed to keep a constant distance between the anode and cathode. Approximately 500kg of carbon is consumed for every tonne of aluminium produced[12]. Originally the anodes were baked in the cell. Pre-baked anodes are now preferred for environmental reasons and better power performance[13].

A pot only produces one tonne of aluminium a day, requiring 4.61 volts[14]. Therefore up to 300 cells can be connected in series in what is called a 'potline'. The high resistance in electrodes, cryolite and anode overvoltage explains large voltage difference between the aluminium production reaction and total voltage.

Voltage distribution.

aluminium production reaction	1.17V	25%
resistance in electrodes	1.08V	23%
resistance in cryolite	1.76V	38%
anode overvoltage	0.60V	13%
total	4.61V	[15]

Large energy losses at the electrodes is due to carbon's high resistance. Carbon is used because it is cheap, solid at 950°C, and isn't corroded by molten aluminium or cryolite.

The resistance of the cryolite can't be reduced as the current passing through the electrolyte generates heat necessary to keep high temperatures and the cryolite molten. If the cryolite was to solidify, the electrolysis reactions would stop.

An anode overvoltage occurs because bubbles of gas are formed at the anode (carbon dioxide). Bubbles have to force the solution apart to grow and then detach from the anode to rise to the surface[16]. This requires extra energy.

Electrical current converted from alternating current (A.C.) to direct current (D.C.), passes from the anodes through the molten cryolite to the cathode lining and steel bar at the base, which carries the current out to the carbon anodes of the next pot.

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[12] Nixon J.C. Aluminium Extraction p19
[13] Nixon J.C. Aluminium Extraction p19
[14] Electrodeposition of Metals
[15] Electrodeposition of Metals
[16] Electrodeposition of Metals

Current passed through the electrolyte causes redox reactions at the electrodes, which wouldn't spontaneously occur. Aluminium (denser than cryolite) deposits as a liquid, as it's melting point is 660°C[17], on the carbon lining forming part of the cathode, and is vacuum-syphoned from each pot regularly for casting. Oxygen formed at the anodes react with the carbon to produced carbon oxides.

Reduction of alumina occurs at the cathode:

$$Al_2O_{3(\text{in cryolite})} + 6e^- \rightarrow 2Al_{(l)} + 3O^{2-}{}_{(g)}$$ [18]

alumina gains electrons to become aluminium

Oxidation of carbon at the anode (reactions are more complex):

$$C_{(s)} + 2O^{2-}{}_{(\text{in cryolite})} \rightarrow CO_{2(g)} + 4e^-$$ [19]

carbon loses electrons and reacts with oxygen ions to form carbon dioxide.

There are also anions AlO_2^- and $AlOF_2^-$, so the use of O^{2-} is a simplification[20].

overall reaction :

$$2Al_2O_{3(s)}+3C_{(s)}\rightarrow 4Al_{(l)}+3CO_{2(g)}$$ [21]

Adding alumina intermittently to the cell replaces alumina decomposed by electrolysis. If the alumina is in excess a sludge forms on the cathode disrupting the current flow[22]. Intermittent feeding and replacement of anodes causes slight temperature alterations resulting in the loss of 'ledge' from cell walls. Ledge is solidified electrolyte protecting walls from corrosion and erosion[23] and also prevents electrolysis occurring at the walls, ensuring a vertical current flow from anodes to cathode.

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[17] Nixon J.C. Aluminium Extraction p19
[18] Ross B. The Chemistry of Aluminium p3
[19] Commons C. Chemistry Two p237
[20] Reactions from electrical energy
[21] Ross B. The Chemistry of Aluminium p3
[22] Nixon J.C. Aluminium Extraction p19
[23] Nixon J.C. Aluminium Extraction p19

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Production & energy efficiency of a Hall-Heroult cell using Faraday's laws of electrolysis.

Faraday's laws:

1. The mass of any substance deposited, evolved, or dissolved at an electrode in an electrochemical process is directly proportional to the amount of electricity passed through the cell. $m \propto Q$
2. For one mole of a substance to be deposited, evolved, or dissolved at an electrode, the passage of one two, three, or another whole number of moles of electrons is required.

Electric charge - Q
Current - I
Volts - V
Time - t
mass - m
Faraday -F
Number of moles of electrons - n(e−)
Molar mass - M

$$Q = I \times t$$

$$Q = n(e^-) \times F$$ [24]

$$m = n \times M$$ [25]

Production

One Faraday = 96 500 coulomb mol^{-1} [26]
Valence (Al) = +3 [27]
Atomic weight (Al) = 26.9815 [28]

$$\therefore Al^{3+} + 3e^- \rightarrow Al_{(l)}$$

According to Faradays second law, 3 moles of electrons are required for the deposition of 1 mole of aluminium.

$$n(Al) = \tfrac{1}{3} n(e^-)$$

$$\therefore m(Al) = \tfrac{1}{3} n(e^-) \times M$$

$$n(e^-) = \tfrac{Q}{F}$$

$$= \tfrac{I \times t}{F}$$

$$\therefore m = \tfrac{I \times t \times M}{3F}$$

let t = 1 day
let I = 150 000amps

$$= \frac{150000 \times 60 \times 60 \times 24 \times 26{\cdot}9815}{3 \times 96500}$$

$$= \frac{3{\cdot}497 \times 10^{11}}{289500}$$

$$= 1207876g$$

$$= 1208kg$$

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[24] Commons C. Chemistry Two p227
[25] Commons C. Chemistry Two p19
[26] Commons C. Chemistry Two p227
[27] Ross B. The Chemistry of Aluminium p10
[28] Commons C. Chemistry Two p361

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Theoretically, a typical cell produces 1208kg of aluminium each day. However in practice, electrical shorting, other electrolytic reactions and some reoxidation of aluminium reduce 'current efficiency' (percentage of current resulting in aluminium being produced) thus reducing aluminium production. Current efficiency for most pots is between 90 & 95%[29].

$$\therefore \text{Actual production (Al)} = 1208 \times \frac{90}{100}$$
$$= 1087kg$$

Volume CO_2

$$2Al_2O_{3(s)} + 3C_{(s)} \rightarrow 4Al_{(l)} + 3CO_{2(g)}$$ [30]

$$n(e-) = \frac{I \times t}{F}$$
$$= \frac{150000 \times 60 \times 60 \times 24}{96500}$$
$$= 134301 mol$$
$$n(Al) = \frac{1}{3} n(e-)$$
$$= \frac{1}{3} \times 134301$$
$$= 44767 mol$$
$$n(CO_2) = \frac{3}{4} \times 44767 \quad \text{(from equation)}$$
$$= 33575 mol$$

$$n = C \times V$$ [31]

molar volume of gas ≈ 24·5 L mol^{-1} (standard laboratory conditions)

$$V = \frac{n}{C}$$
$$\approx \frac{33575}{24.5}$$
$$\approx 1370\text{L per cell per day.}$$

Energy Efficiency

Average voltage for a cell 4.61V

energy = V × I × t[32]

$$= 4.61 \times 150000 \times 60 \times 60 \times 24$$
$$= 5{\cdot}97456 \times 10^{10} J$$
$$= 59745600 kJ \text{ per cell}$$

$$\text{energy consumption kWh/kg} = \frac{(V \times I) \times t}{1000 \times m(Al)}$$
$$= \frac{150000 \times 4{\cdot}61 \times 24}{1000 \times 1087}$$
$$= 15{\cdot}27 \text{kWh/kg}$$

Average energy efficiency of a Hall-Heroult cell is 15.27kWh/kg

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[29] Alcoa Australia [Student notes]

[30] Ross B. The Chemistry of Aluminium p3

[31] Commons C. Chemistry Two p

[32] Commons C. Chemistry Two p201.

Environmental implications

Aluminium smelters operate under strict conditions of a Clean Air Licence[33]. Hydrogen fluoride is formed by hydrolysis reactions between cryolite and atmospheric moisture[34] shown in the equation below.

$$2Na_2AlF_6 + 3H_2O \rightarrow Al_2O_3(s) + 6NaF(s) + 6HF(g)$$

The pot is enclosed to reduce these emissions, which are piped to a dry scrubbing plant. Fluorides are then passed through alumina and absorbed. The alumina is re-cycled into the cells, so 99% of fluoride is prevented from reaching the atmosphere[35]. Fluorides formed in production of carbon anodes are also recycled into the smelting process.

Another by-product from aluminium smelting is spent potlining (SPL). The carbon lining reacts with air to form cyanide and absorbs fluorides and sodium salts from the electrolyte. SPL is heated to 700°C to break down cyanide into nitrogen and carbon dioxide. The fluorides are recovered from the ash, the residue passes leaching tests and is considered non-toxic.[36]

Because electricity is used as an energy source for the electrolysis of aluminium, environmental implications from the source should also be considered. Different plants use different sources of energy, most Australian plants are coal-fired[37]. Coal-fired plants release sulfur dioxide into the atmosphere which reacts with moisture forming acid rain. This can have devastating effects on forests, animals and even buildings. Cooling water released from the power stations causes thermal pollution. The water heats the lake or river in which it is released effecting fish and other aquatic species[38]. Also associated with coal burning is the release of carbon dioxide and carbon monoxide which contribute to the green house effect.

My calculations show that approximately 1370L of carbon dioxide is released from each cell every day which also contributes to the green house effect. I assumed standard laboratory conditions for my calculations however, these are different to the actual conditions where the reaction occurs, so the figures are only a rough approximation.

Technological and economic implications

Aluminium smelting requires large amounts of energy, 59 745 600kJ for a cell. Even small improvements to the process saves the industry millions of dollars. Smelters are located on low energy cost sites. Increases in energy costs have encouraged improved efficiency and increased plant size[39].

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[33] The Australian Aluminium Industry [Booklet] p17
[34] Ross B. The Chemistry of Aluminium p5
[35] ALCOA Australia [Booklet] p27
[36] Comalco works to solve a universal headache
[37] Production of Aluminium In Electrolytic Cells p3
[38] Commons C. Chemistry Two p184
[39] Production of Aluminium In Electrolytic Cells p1

Major companies are able to develop more efficient methods by having each plant investigate a specific parameter such as raw material supply costs, delivery schedules or preparation of each of the process inputs[40]. The services of chemists, computer scientists, electrical engineers and accountants are often employed.

Although the process has been well developed, practical efficiency of smelting (shown previously 15.27kWh/kg) is not as efficient as theoretical levels 6.3kWh/kg[41]. Research into the aluminium industry would increase productivity, improve environmental controls and allow the development of techniques using smaller amounts of electricity. The export of this technology could earn lots of money for Australia.

Conclusion

Aluminium is produced by electrolysis in a Hall-Heroult cell. Electricity travels from the suspended anodes through the cryolite electrolyte to the carbon lining of the pot which acts as the cathode. Electricity then passes from the cell through a steel bar at the base and into the anodes of the next pot. This process reduces alumina to aluminium which deposits on the cathode and is syphoned off for casting.

The process has been extensively developed since 1886 and although there is room for improvements in efficiency and the environmental effects of the electricity source, smelting itself is relatively clean and there are few environmental concerns. Not only does the export of aluminium earn money for Australia but there's potential for research into more efficient techniques to be sold or leased to other companies world wide.

Evaluation of Information

The sources generally supported each other, indicating that the information was accurate. The reaction occurring at the anode is simplified, as this is the one used by most reference material and I couldn't find a more accurate representation. The energy efficiency and voltage and current passed through the cell, obviously depend on the particular plant, so any calculations are approximate and apply to a typical cell only. Most of the information used was obtained from companies who smelt aluminium. They would be promoting a desirable image and thus may be biased in the extent of damage caused to the environment. An independent report or 'green' group may lead to different conclusions about the impact on society.

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[40] Production of Aluminium in Electrolytic Cells p2
[41] Nixon J.C. Aluminium Extraction p20

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